

Comparison of GC/MS Methods for the Measurement of Brominated Diphenylethers (PBDEs) in Food Samples

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Introduction.

The determination of brominated biphenyl ethers (PBDEs) with high bromine content is quite often an analytical problem. The physical and chemical properties of BDE-209 put great demands on the analytical method including sampling, extraction and clean up, as well as final chromatographic separation. The problems encountered during the analysis of high molecular weight BDE congeners are associated with thermal instability, rather than their high boiling points. The degradation of particularly BDE-209 is increased with temperatures, time spent at elevated temperatures and presence of catalytic sites. For best yield of the deca-brominated congener these parameters should be kept as low as possible. The gas chromatographic separation of PBDEs is often performed on two separate columns, one for the low molecular weight BDE congeners using a 30-60 m long column, while the analysis of the high molecular weight BDE-209 is performed on a shorter column of e.g. 10 m length.

Björklund et al. (2003) demonstrated that columns with supposedly similar stationary phases may result in a large difference in the yield of PBDEs. Furthermore, losses of high molecular weight BDE-congeners do occur in the GC column and are correlated to the column length and the stationary film thickness. Time, temperature and catalytic sites all contribute to reduce the yield of the high molecular weight congeners (Covaci et al., 2003, Dirtu et al., 2008, van Leeuwen and de Boer, 2008). To obtain a high yield of these congeners, especially BDE-209, short inert columns with a thin stationary phase are preferred.

Materials and Methods.

We recently analyzed 31 pooled food samples collected in 2008/2009 in the United States. The analytical data for PBDEs and a number of other contaminants have been reported recently. (Schechter et al., 2009, 2010) The samples have been measured by 3 different techniques as can be seen in **Table 1**. All methods reported here followed the isotope dilution technique.

Twenty four (24) native standards (BDE Nos. 17, 28, 47, 49, 66, 71, 77, 85, 99, 100, 119, 126, 138, 153, 154, 156, 183, 184, 191, 196, 197, 206, 207, 209) were obtained from Wellington Laboratories, Canada. Nine (9) internal ¹³C₁₂ - labeled standards - BDE Nos. 28, 47, 99, 138, 153, 183, 196, 207 and 209 - were delivered by Wellington, Canada. The number of 28 individual congeners is relatively large. The measurements here are only reported for the 14 predominant PBDEs mainly applied as internal standards.

Clean up of all lipid extracts was performed by acid treatment and alumina oxide column (Schechter et al., 2009). The final extract was reduced in volume by a stream of nitrogen, the final volume was 50 µl containing ¹³C₁₂ - labeled BDE 138 as recovery standard. Typical recoveries found for the methods used range between 65 and 130 %.

We applied High Resolution Mass Spectrometry, HRMS, Thermo Finnigan, (**method 1**) and Low Resolution Mass Spectrometry, LRMS, HP5973, (**method 2**) using electron impact (EI) as ionization technique for both. The third technique used was Low Resolution Mass Spectrometry, LRMS, HP5973, (**method 3**) using negative ionization (NCI). This technique is applied mostly for measurement of bromine containing organic substances by tracing only the isotopes of bromine: m/e 79 and 81. In contrast to the common application measuring only bromine we followed a different approach. With the actual procedure we did measure the highly brominated components (Octa-, Nona- and DecaBDE) by tracing the relevant M and/or (M-2 Br) ions.

Table 1: GC/MS measurements of food samples

Method No	Type	Instrument	Ionization Technique	Conditions Gas chromatograph	Conditions Mass spectrometer
1	GC/HRMS	Trace Ultra GC/DFS	EI ¹	Split-less; injector: 290 °C Oven Temp.: 90 > 300 °C DB 1, 12 m, 0,18 mm ID, 0,18 µm	R: 10 000 Source Temp.: 290 °C EV : 45
2	GC/LRMS	HP 6890/ HP5973	EI	Split-less; PTV injector: 150 > 280 °C Oven Temp.: 150 > 320 °C DB 5, 25 m; 0,25 mm ID; 0,1 µm	R: nominal Source Temp.: 230 °C EV : 70
3	GC/LRMS	HP 6890/ HP5973	NCI ²	Pulsed-split less; injector: 280 °C Oven Temp.: 90 > 300 °C DB 5; 15 m; 0,25 mm ID; 0,1 µm	R: nominal Source Temp.: 150 °C Quad Temp.: 106 °C EV : 235

¹ EI = electron impact, ² NCI = negative chemical ionization, reactant gas: methane

The measurements were performed using three different types of mass spectrometry conditions. In addition to this we applied different columns and different conditions for the gas chromatograph. For **method 1** we used a short DB 1 column with small inner diameter (ID) of only 0,18 mm and a relative thick layer of the stationary phase of 0,18 µm. For **method 2** we used a medium long DB5 column with “normal” ID of 0,25 mm and stationary phase of 0,1 µm. For **method 3** we used the same column like for **method 2** with exception of the length. Here the length was only 15 m.

With respect to the injection technique we used for **method 1** a normal split less injector, for **method 2** a PTV split less injector and for **method 3** a pulsed split-less injector.

Results and Discussion.

The measurements using three different techniques were performed for each of the 31 food samples. We selected a number of 5 typical samples presented in **Table 2**. As can be seen from the table all 14 congeners were measured with **method 1** and **method 2**. For reason of acceptable GC separation of the individual PBDE congeners we analyzed only the OctaBDEs, NonaBDEs and DecaBDE with **method 3**. Due to the GC conditions we observed very short retention time for the components in question resulting in very sharp peaks producing an increase of sensitivity.

Comparing the results received with the different techniques applied it is our impression that the combination of **method 1 and 3** is most suitable with respect to the best sensitivity. For NonaBDE and DecaBDE the best sensitivity is achieved by **method 3**. The observed increase of sensitivity reaches a maximum of up to about 10 fold. On the other hand we see relatively similar sensitivity in some samples for some of the highly brominated congeners measured by the different methods. Comparing the analytical data received by use of the three techniques we observe a good correlation between the congeners measured with each method. We applied these three types of measurements available in our laboratory for the measurement of 31 food samples. In continuation of the project we have plans to include additional basic work.

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Table 2: Typical examples for PBDE measurements using three different GC/MS methods, all values are given in pg/g, wet weight

		Fresh Salmon			Butter			Canned Tuna			Margarine			Olive Oil		
Lipid content (%)		11,9			91,4			14,8			79,4			> 99		
		1 ¹	2 ²	3 ³	1	2	3	1	2	3	1	2	3	1	2	3
BDE-17	TriBDE	9,7	8,5		nd (3)	nd (1)		nd (0,2)	nd (0,2)		nd (3)	nd (3)		nd (3)	nd (2)	
BDE-28	TriBDE	30	28		nd (3)	5,3		0,59	nd (0,2)		nd (3)	nd (2)		nd (3)	nd (2)	
BDE-47	TetraBDE	456	486		186	173		9,1	9,0		16	15		18	15	
BDE-49	TetraBDE	na	139		na	nd (3)		na	2,7		na	nd (3)			nd (3)	
BDE-99	PentaBDE	69	70		165	157		2,3	2,0		33	29		15	9,9	
BDE-100	PentaBDE	96	96		31	24		3,0	3,1		8,5	nd (2)		nd (5)	nd (3)	
BDE-153	HexaBDE	16	16		25	17		nd (0,6)	1,0		nd (9)	nd (4)		nd (8)	nd (4)	
BDE-154	HexaBDE	42	49		12	5,4		1,8	1,9		nd (8)	nd (3)		nd (7)	nd (3)	
BDE-183	HeptaBDE	1,6	nd (2)		nd (9)	nd (8)		nd (0,8)	nd (1)		nd (11)	nd (5)		nd (11)	nd (7)	
BDE-196	OctaBDE	nd (2)	nd (4)	nd (1)	nd (13)	nd (14)	14	nd (1)	nd (3)	nd (1)	nd (16)	nd (20)	nd (6)	nd (14)	nd (15)	nd (6)
BDE-197	OctaBDE	nd (1)	nd (4)	nd (1)	32	nd (14)	11	nd (1)	nd (2)	nd (1)	nd (17)	nd (19)	nd (6)	nd (15)	nd (14)	nd (6)
BDE-206	NonaBDE	nd (4)	nd (20)	nd (3)	316	260	224	nd (3)	nd (8)	nd (1)	nd (41)	nd (119)	nd (11)	nd (37)	nd (82)	nd (13)
BDE-207	NonaBDE	nd (5)	nd (14)	n.d. (3)	381	395	359	nd (4)	nd (6)	nd (1)	nd (57)	nd (84)	nd (11)	nd (43)	nd (58)	nd (13)
BDE-209	Deca BDE	46	nd (123)	7,2	5408	6430	5190	19	nd (16)	nd (16)	nd(89)	nd (832)	nd (57)	508	nd (755)	nd (65)

¹) 1: HRMS , EI, ²) 2:LRMS, EI, ³) 3: LRMS, NCI, nd = not detected, () = detection limit, na = not available